

Final Report for FA2386-11-1-4100 "Carbon-coated current collectors for high-power Li-ion secondary batteries"

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Abstract: The ultimate goal of this project is to develop a viable C-coating process of the current collector in order to improve the overall power performance of the electrode of Li-ion batteries. During this second-year period, study has been focused onto the development of a low-temperature chemical vapor deposition (PA-CVD) process for C deposition. The PA-CVD vacuum chamber has been set-up. We have completed the investigation of the effects of the processing parameters, on the characteristics of the C layer will be studied. The surface properties of the C layer, including morphology, surface roughness and composition, have been characterized with several surface analysis techniques including X-ray photoelectron spectroscopy, scanning electron microscopy (SEM) and atomic force microscopy (AFM). A rather uniform thin layer of C-coating has been achieved on Al foil of 20- μm thick under continuous deposition condition. Surface analysis indicates that this thin C layer does not contain interfacial Al-carbide layer. LiFePO₄ electrode using this C-coated Al current collector exhibits higher capacity under 10 C rate and much more the cycle life under the 2C-charge/5C discharge cycling, as compared with its counter-part without the C coating.

Introduction:

The basic principle for achieving high-power capability of a battery is minimizing the overall resistance of the electrochemical system. For Li-ion batteries, much research effort has been devoted in the past to minimize the ionic diffusion resistances and electronic resistance associated with the electrode active materials. In the typical electrode configuration, the layer containing the active material is supported on a metallic current collector. The interface between the current collector and active layer imposes additional resistance to charge transfer within the electrode. This resistance source has not received sufficient attention in the past, presumably because it was not considered of significance for the low-power Li-ion electrode materials. However, the advancement in the material synthesis technologies has reduced the ionic and electronic resistances associated with the active materials to certain point that they become competitive to the other resistance sources. Thus, the significance of the electronic resistance at the active layer/current collector (AL/CC) interface is worthy of careful re-examination.

The objects of this study is to prepare C-coated Al current collectors by two different coating processes, including high-temperature thermal chemical vapor deposition (HT-CVD) and low-temperature chemical vapor deposition (PA-CVD), and to characterize their electrochemical properties pertain to the power performance and cycling stability of Li-ion batteries. At least two beneficial effects are anticipated to result from the C-coating. For one, the C-coating removes the native surface oxide layer on the metal current collectors. For the other, the C-layer is hydrophobic in nature and hence helps to improve the interfacial bonding. Both effects are expected to reduce the AL/CC interfacial resistance. The ultimate

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| 14. ABSTRACT The ultimate goal of this project is to develop a viable C-coating process of the current collector to improve the overall power performance of the electrode of Li-ion batteries. During this period, study was focused onto the development of a low-temperature chemical vapor deposition (PA-CVD) process for C deposition. The PA-CVD vacuum chamber was set-up. The researchers completed the investigation of the effects of the processing parameters; the characteristics of the C layer will be studied later. The surface properties of the C layer, including morphology, surface roughness and composition, were characterized with several surface analysis techniques including X-ray photoelectron spectroscopy, scanning electron microscopy (SEM), and atomic force microscopy (AFM). A rather uniform thin layer of C-coating was achieved on 20-μm thick Al foil under continuous deposition conditions. Surface analysis indicated that this thin C layer does not contain an interfacial Al-carbide layer. LiFePO4 electrode using this C-coated Al current collector exhibits higher capacity under 10 C rate and much more the cycle life under the 2C-charge/5C-discharge cycling, as compared with its counter-part without the C coating. | | | | | |
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goal is to develop a viable C-coating process of the current collector in order to improve the overall power performance and/or cycle life of the electrode of Li-ion batteries. During this second-year period, study has been focused onto the development of a PA-CVD process for C deposition.

Experiment:

Surface and electrochemical analyses

The surface composition at different depth was analyzed by X-ray photoelectron spectroscopy (XPS), which employed an Al K α X-ray source operated at 15 kV and 100 W, and used a beam size of 400 μ m and a pass energy of 20 eV for spectrum acquisition. Sputtering gun was operated at 3 kV and 1 μ A with a sputtering area of 2 mm x 2 mm. The surface hydrophobic property was determined by contact angle test (FTA105) with DI water. Raman spectrum was used to analyze the structure of carbon layer, and the wave length of laser light source is 532nm. Conductive atomic force microscope (CAFM) was used to measure the surface morphology and conductivity distribution on the Al surface.

Electron-performance for use modified Al foil as current collector of the cathode. LiFePO₄ (LFPO) was used as active materials for test, and this cathode material was purchased from Aleees company. The LFPO active layer contains 85 wt.% LFPO powder, along with 7wt% carbon conducting additives and 8wt% polymeric binder (Polyvinylidene difluoride; Aldrich). The electrodes were roll-pressed and finally dried at 150 °C for 6 hr in vacuum. The resulting LFPO electrodes have a weight of ca. 2.50 mg/cm². The electrodes were assembled with Li-foil counter electrodes to make CR2032 coin cells, and the electrolyte was 1 M LiPF₆ in a 1:2 v/v mixture of ethylene carbonate (EC) and ethyl methyl carbonate (EMC; Mitsubishi Chemical). All the cells were assembled in a dry room where the dew point was maintained at between -40 and -45 °C.

Electrochemical characterizations include constant current charge/discharge (C/D) test and electrochemical impedance spectroscopy (EIS). The C/D tests were carried out with selected current rates on a battery tester (Arbin, model: MCN6410). The charge and discharge phases of a cycle were always conducted at the same selected current rate. EIS analysis (AUTOLAB, Eco Chemie PGSTAT30) was conducted with the frequency ranging from 10 mHz to 60 kHz and a voltage amplitude of 10 mV at the open-circuit voltage (OCV) of a cell.

Results and Discussion:

The photo of Al foil and treated Al are shows in Fig. 1. The color of the Al foil was change from sliver like to brown after the treatment. However, the one annealed with better isolation to the oxygen kept the brownish color.

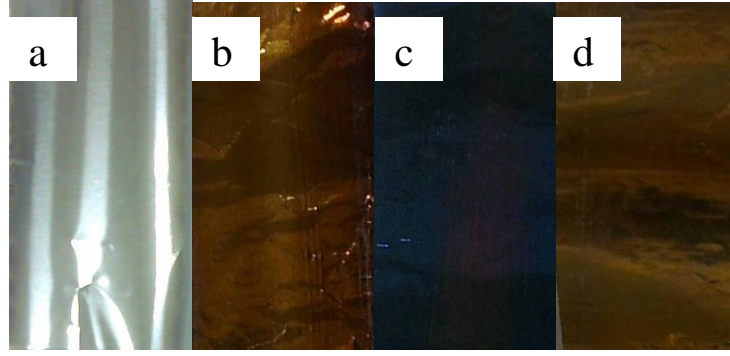


Figure 1. the photo of Al foil(a) and treated Al(b-d).

Surface analyses

XPS results of Al, and two treated Al are shows in Fig. 2(a-c), Fig. 3(a-c) and Fig. 4(a-c) respectively, and we can use the signal change of Al, O and C with different sputtering time to determine the composition at different depths from surface. For fresh Al foil, the Al($2p^{3/2}$) spectrum shows the surface having an alumina oxide lay, and the signal of alumina oxide decreases, while Al metal peak increases and the O peak in O(1s)spectrum decreases. The intensity of the Al metal peak gets steady when increasing sputter time to 5 mins, so we can roughly determine the thickness native oxide lay at Al surface to be about 50 nm.

First treated sample (Fig. 3 a-c), only carbon can be detected on the surface before sputtering for 10 min and the thickness of this carbon layer can be roughly estimated around 300 nm. Except for the initial C signal before sputtering, which might be due to contamination, the C single at lower depth always shows a lower binding energy, which may be attributed to bonding with hydrogen. Further increasing the sputtering time to exceed 10mins, the intensity changes of Al and O signals are similar to those of fresh Al foil except for lower intensity of O. All XPS results for the first treated Al indicates slight removing of oxide lay and the formation of surface carbon layer containing hydrogen.

For the XPS results of second treated sample (Fig. 4a-c), one of the essential difference is the position of binding energy of carbon. From C(1s),the binding energy increase to 284ev which is the normal binding energy of graphite. So we can infer the second process can help to remove hydrogen as well as transform the C layer to be more graphitic-like. However, from O(1s), the intensity of oxygen also rise up at a quite deep region.

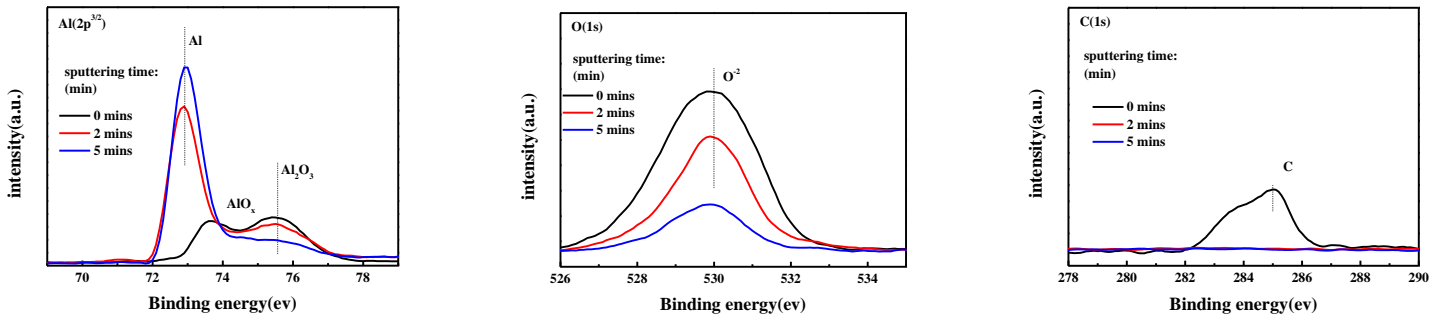


Figure 2(a-c). XPS spectrum of Al foil in different orbital. Al($2p^{3/2}$)(a),O(1s)(b) and C(1s)(c).

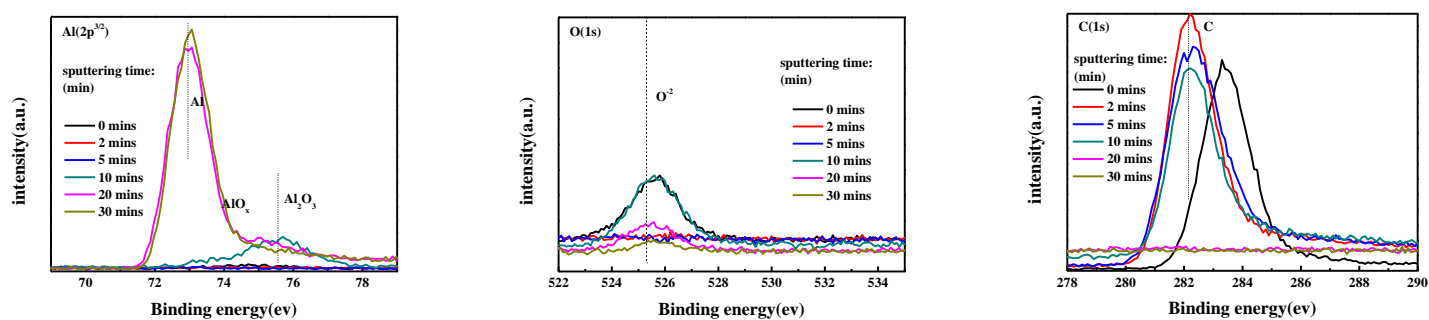


Figure 3(a-c). XPS spectrum of first treated foil in different orbital. $\text{Al}(2p^{3/2})$ (a), $\text{O}(1s)$ (b) and $\text{C}(1s)$ (c).

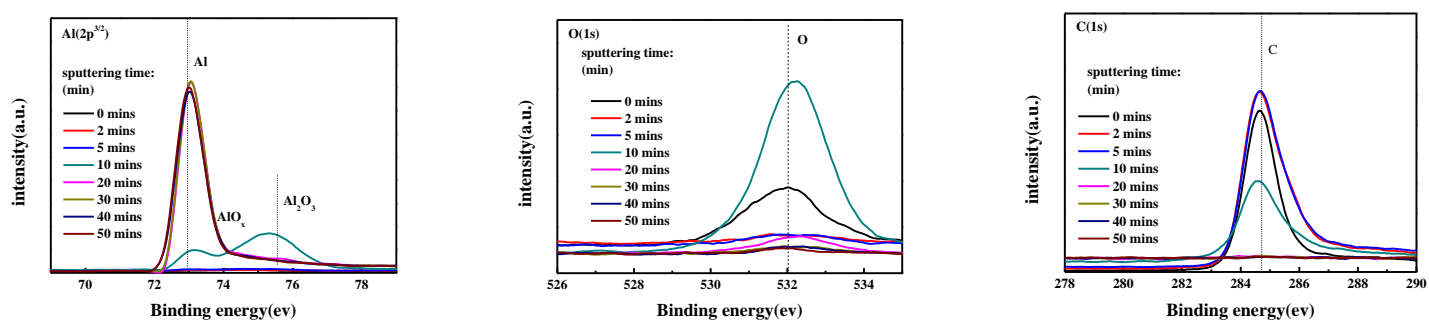


Figure 4(a-c). XPS spectrum of second treated foil in different orbital. $\text{Al}(2p^{3/2})$ (a), $\text{O}(1s)$ (b) and $\text{C}(1s)$ (c).

The contact angle images of water are shown in Fig. 5(a-d) and the data are summarized in Fig. 6. The contact angles are in the order of first treated Al > second treated Al > Al . It is very clear that the contact angle increases after the process due to the carbon coating. Both treated samples have higher contact angles, corresponding to more hydrophobic surface, which can be expected to have better contact with the active layer, which is also hydrophobic.

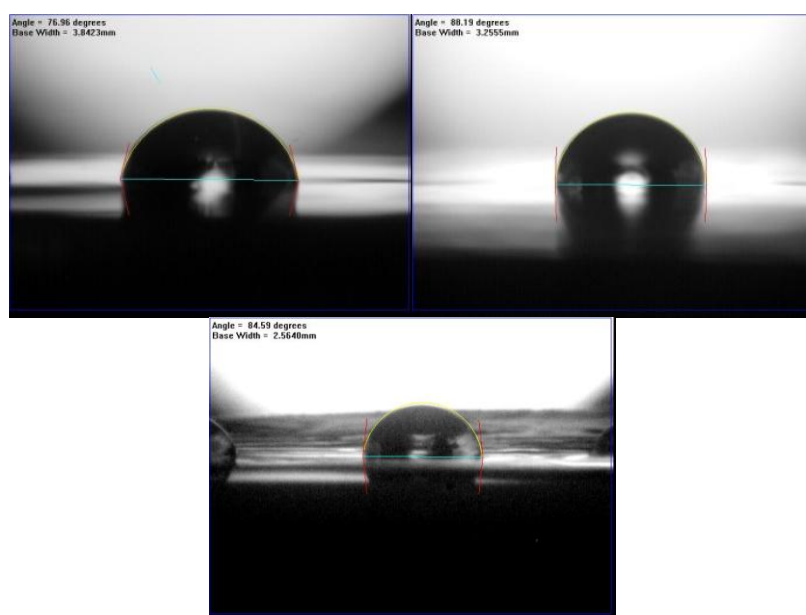


Figure 5(a-d). contact angel of Al (a), first treated(b), second treated Al (c).

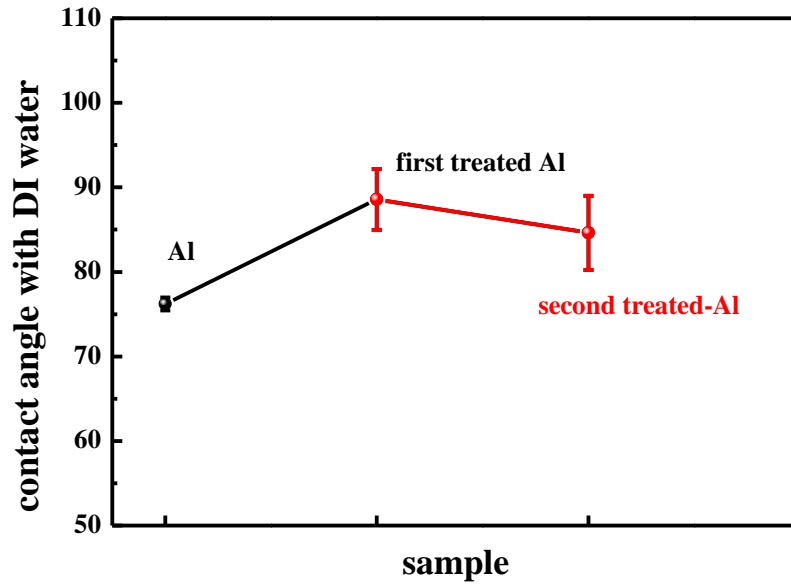
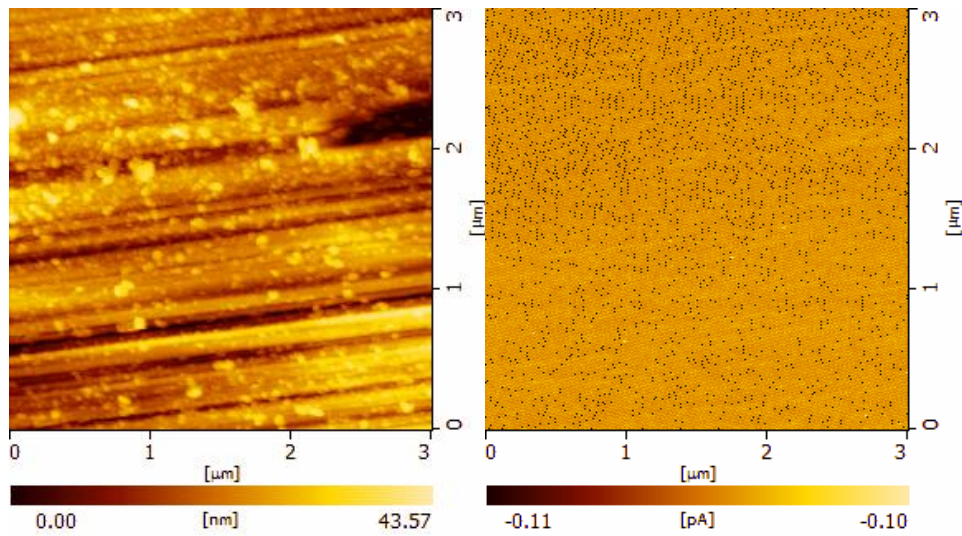


Figure 6. the diagram of contact angle of different Al foil.

Conductive atomic force microscope (CAFM) can give us some information about the surface morphology and conductivity distribution on the surface. Keeping the potential of the conductive tip at 3V, the images of height and images of current passing through the tip are shown in Fig.7 (a-d), where we compare the surface of Al and second treated Al. From the surface morphology images, it can be found that, after the coating treatment, the surface shows granules, and the surface roughness increases from 5.23nm to 9.61nm. From the image of the current distribution, the Al foil can only get tiny amount of current, and it might due to the isolation of native oxide layer. The second treated Al shows some high current areas. These high current areas have much better conductivity than the Al surface, and it can help electron transferring from the active layer to the current collector.



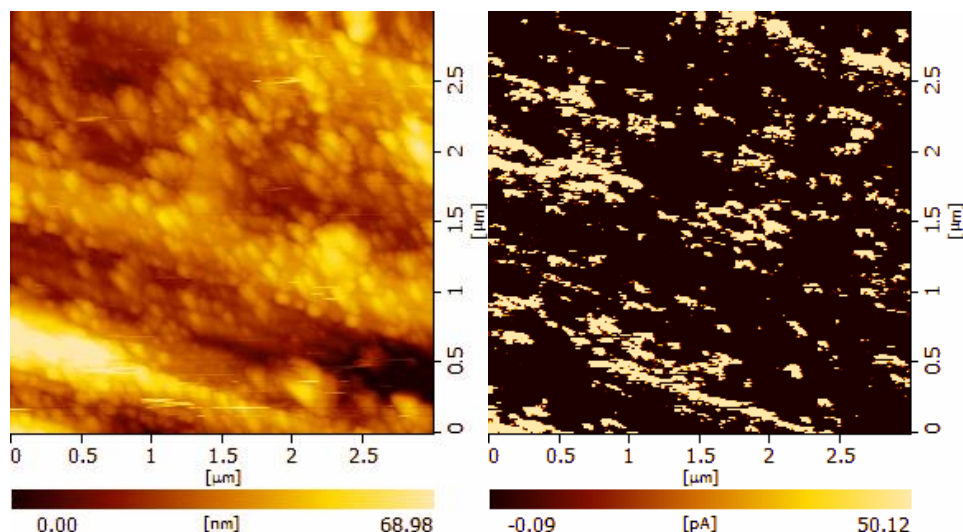


Figure 7(a-d). AFM image of Al(a) and second treated Al(c) surface, and CAFM image of Al(b) and second treated Al(d) surface.

Electrochemical Analyses

The performance of the LFPO electrodes using these current collectors has been compared. The rate capacities of the electrodes with three kinds of current collectors were shown in Fig. 8. It shows the rate capacity of LiFePO_4 (LFPO) dramatically decreases when using first treated Al as current collector. In contrast, the rate capacity can increase when the second treated Al is used as current collector, but the extent of enhancement for capacity is small and only at high C-rate (>10 C). However, the resistance effect from different current collectors can be obviously observed from the charge/discharge voltage curves (Fig. 9). The electrode with second treated Al current collector shows the least polarization at 10C than the other two. Another important difference in electrochemical performance is that the electrode using the second treated Al current collector shows much improved cycle life than that using the bare Al (Fig. 10). This may be because high resistance at the interface of active material and current collector may damage the stability of this electrode, and the use of the second treated Al current collector giving lower interfacial resistance can decrease the fading rate of the electrode.

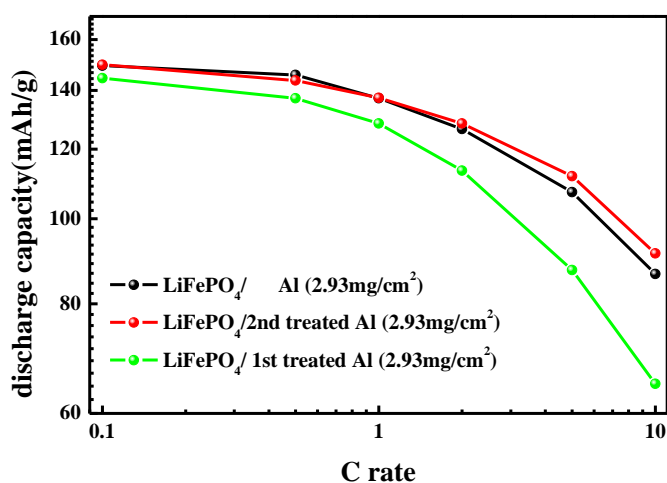


Figure 8. Rate capacity of LFPO electrode with different current collector.

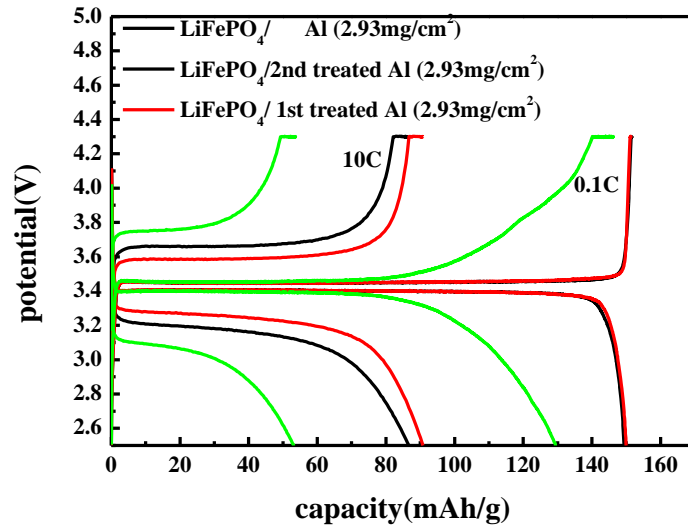


Figure 9. Charge discharge curve of LFPO electrode with different current collector at 0.1C and 10C.

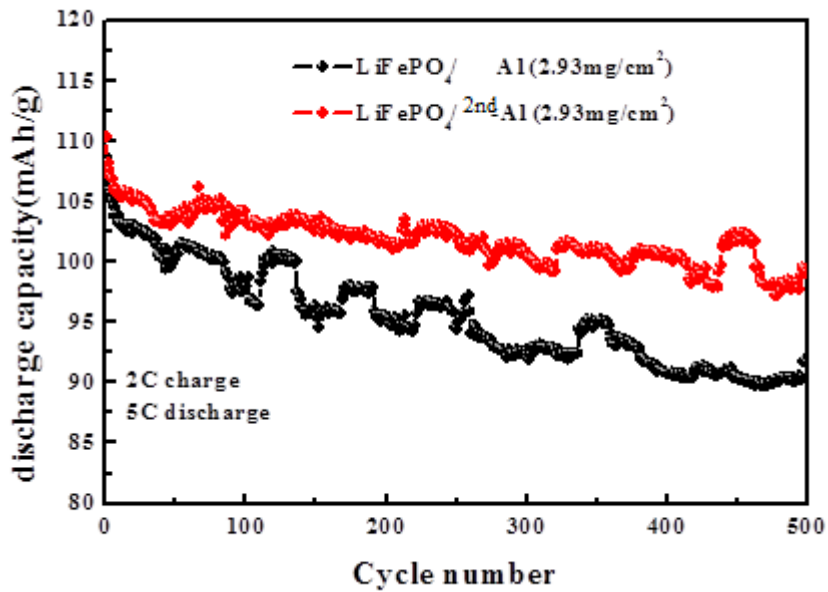


Figure 10. cycle performance of LFPO electrode with different current collector.

Conclusion

For the 2nd treated C-coated Al, there is some high conductive regions penetrating through the native alumina oxide layer, and a high conductive carbon coating on the surface makes the surface hydrophobic. When use it as current collector, hydrophobic surface can increase the contact of the surface of active material and current collector, and the electron transfer can simultaneously be enhanced. This low resistance successfully result in better rate capacity, low polarization and better cycle life.

List of Publications:

Publication:

Hsien-Chang Wu, Eric Lee, Nae-Lih Wu^{*}, and T. Richard Jow, "Effects of Current Collectors on Power Performance of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ Anode for Li-Ion Battery," J. Power Sources, in press (2011).

Presentation:

2012 International Battery Association meeting, "Current collector issues for Highrate performance of Li-ion Battery electrodes," January 9-13, Waikaloa, Hawaii.